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Phase Space Structures Explain Hydrogen Atom Roaming in Formaldehyde Decomposition

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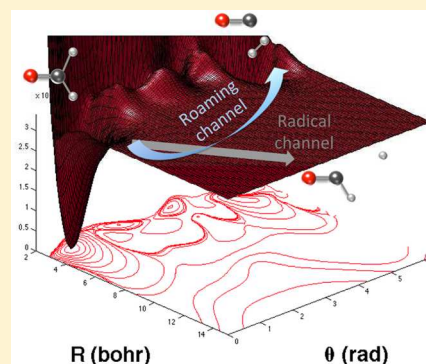
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S Supporting Information

ABSTRACT: We re-examine the prototypical roaming reaction—hydrogen atom roaming in formaldehyde decomposition—from a phase space perspective. Specifically, we address the question “why do trajectories roam, rather than dissociate through the radical channel?” We describe and compute the phase space structures that define and control all possible reactive events for this reaction, as well as provide a dynamically exact description of the roaming region in phase space. Using these phase space constructs, we show that in the roaming region, there is an unstable periodic orbit whose stable and unstable manifolds define a conduit that both encompasses all roaming trajectories exiting the formaldehyde well and shepherds them toward the $\text{H}_2\cdots\text{CO}$ well.



A significant challenge to conventional understanding of reaction mechanisms is provided by the recently discovered class of roaming reactions. The roaming mechanism was identified in 2004 in a study of the photodissociation of formaldehyde.¹ When excited by photons of energy greater than 30300 cm^{-1} , the formaldehyde molecule can dissociate via two channels: $\text{H}_2\text{CO} \rightarrow \text{H} + \text{HCO}$ (radical channel) or $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$ (molecular channel). Above the threshold for the $\text{H} + \text{HCO}$ dissociation channel, the CO rotational state distribution exhibits an intriguing “shoulder” at lower rotational levels correlated with a hot vibrational distribution of H_2 coproduct.² The observed product state distribution is not in accord with the traditional picture of the dissociation of formaldehyde via the well-characterized saddle point transition state for the molecular channel. Instead, a new pathway is followed that is dynamical in nature, and such dynamical reaction paths or roaming mechanisms are the central topic of this Letter.

For the case of formaldehyde photodissociation, classical trajectory simulations establish that the roaming manifests itself by a hydrogen atom nearly dissociating and orbiting the HCO fragment at long distances before returning to abstract the other hydrogen and form the molecular products H_2 and CO .¹ Long-range interactions between dissociating fragments allow for reorientational dynamics that can result in a different set of products and/or energy distributions than the one expected from a reaction following the minimum energy path (MEP),

while a dynamical bottleneck prevents facile escape of the orbiting H atom.

Following this work on formaldehyde, roaming has been recognized as a ubiquitous phenomenon in unimolecular decomposition^{3–6} and has been identified in a variety of different types of reactions. Examples of known roaming reactions now include those involving excited electronic states⁷ or isomerization.^{8,9} These studies have identified general characteristics of the roaming mechanism and also highlight the need to extend existing theories of chemical reactions.

The standard picture in reaction dynamics is firmly based on the concept of the reaction coordinate,¹⁰ for example, the intrinsic reaction coordinate (IRC). The IRC is a MEP in configuration space that smoothly connects reactants to products and, according to conventional wisdom, it is the path that a system follows (with small fluctuations) as reaction occurs. Broadly speaking, reactions occurring via the roaming mechanism avoid the IRC and follow alternative reaction pathways. Reactions involving dynamics that avoid the IRC, so-called non-MEP reactions, were extensively studied before the term “roaming” was coined.^{11–16}

A central ingredient of standard reaction rate theories such as transition state theory (TST) is the concept of a dividing

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surface (DS), which is a surface that the system must cross in order to pass from reactants to products (or the reverse).^{17–19} Association of transition states with saddle points on the potential energy surface (PES) has a long history of successful applications in chemistry and has provided great insight into reaction dynamics.^{20–22} Accordingly, much effort has been devoted to connecting roaming reaction pathways with the existence or nonexistence of putative “roaming” saddle points on the PES.^{23,24}

However, in cases where reactions proceed without a clear correlation to PES features such as IRCs or saddles, as appears to be the case for several roaming examples, they are mediated by transition states that are dynamical in nature, that is, phase space structures. The phase space formulation of TST has been known since the beginning of the theory¹⁷ but has only recently reached conceptual and computational maturity for systems with more than two degrees of freedom.²⁵ Fundamental to this development is the recognition of the role of phase space objects, namely, normally hyperbolic invariant manifolds (NHIMs),²⁶ in the construction of relevant DSs for chemical reactions. The NHIM approach to TST has enabled a deeper understanding of reaction dynamics for systems with many (≥ 3) degrees of freedom (DoF).^{25,27,28} For dynamical systems with two DoF, the NHIMs are just unstable periodic orbits (POs), which have long been known in this context as periodic orbit dividing surfaces (PODS).¹⁹

A characteristic of many systems exhibiting roaming reactions studied so far is the presence of long-range interactions between the fragments of the dissociating molecule. This characteristic is typical of ion–molecule reactions, and roaming is clearly expected to be at play in these reactions. The simple model introduced by Chesnavich²⁹ has all of the ingredients required to manifest the roaming effect. In recent studies,^{30–32} we have revisited the Chesnavich model for ion–molecule reactions²⁹ in light of recent developments in TST. We have shown that, for barrierless systems such as ion–molecule reactions, the concepts of orbiting transition state (OTS) and tight transition state (TTS) (see ref 33 and also the unified statistical theory of Miller³⁴) can be clearly formulated in terms of well-defined phase space geometrical objects. (For recent work on the phase space description of OTS, see ref 35.) We demonstrated how OTS and TTS can be identified with well-defined phase space dividing surfaces attached to NHIMs.

In the present Letter, we re-examine the prototypical roaming reaction—hydrogen atom roaming in formaldehyde decomposition—from a phase space perspective. Specifically, we address the question “why do trajectories roam rather than dissociate through the radical channel?” Roaming has been found in formaldehyde for total energies from below to above the threshold to radical products,³⁶ so that a fundamental understanding of the roaming mechanism requires elucidating why some trajectories do not follow a path leading directly to the radical products, even when they have enough energy to do so. In this work, we describe and compute the phase space structures that define and control all possible “reactive events” for this reaction, as well as provide a dynamically exact description of the “roaming region”.

To investigate roaming dynamics in formaldehyde decomposition, we use a reduced 2 DoF model. The model assumes that the HCO fragment is a rigid body and describes the dynamics of the other hydrogen atom moving with respect to the HCO fragment restricted to a plane. The angle θ describes

the orientation of the hydrogen atom with respect to the HCO fragment, and the radial coordinate R describes the distance from the center of mass of the HCO fragment to the hydrogen atom. The Hamiltonian for this model is obtained by deriving an expression for the kinetic energy for motion in the plane in terms of the conjugate momenta p_θ and p_R (and the total angular momentum J , set equal to zero, $J = 0$) and by constructing a potential energy function $V(R, \theta)$ from the full six-dimensional PES produced by Bowman.³⁷ The Hamiltonian as well as the way that the PES was obtained are described in the Supporting Information (SI) accompanying this Letter. The PES and the coordinate system used are shown in Figure 1.

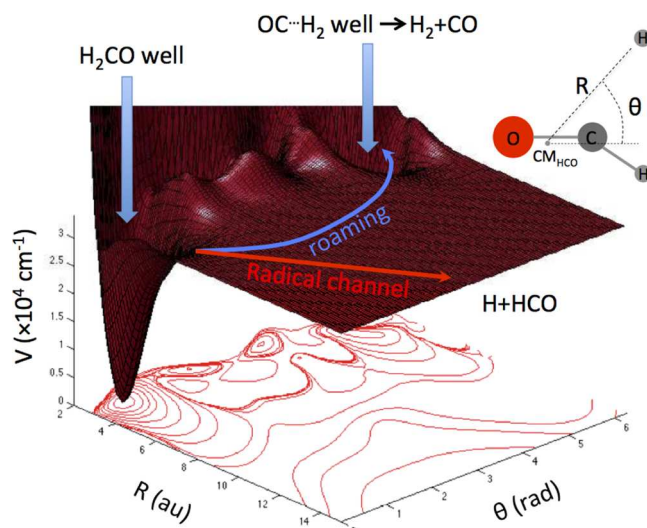


Figure 1. Two DoF potential energy surface and coordinates employed in the reduced dimensional model.

This model describes the long-range part of the potential, and it is appropriate for investigating the dissociation of formaldehyde into the radical products $H + HCO$ (indicated by the R coordinate becoming large) as well as the molecular product channel $H_2 \cdots CO$.

The roaming phenomenon is manifested as follows. Trajectories initiated in the formaldehyde well leave the well and follow a path to dissociation to the radical products $H + HCO$. However, in the course of their evolution, the roaming trajectories deviate from this path, and the hydrogen atom rotates around the HCO fragment before binding with the other hydrogen atom and finally dissociating to $H_2 + CO$.

In order to analyze the questions raised above, we first identify the relevant “reactive events” and then determine the unstable POs (NHIMs for 2 DoF systems) from which we construct DSs, the crossing of which defines these reactive events. In one relevant reactive event, the formaldehyde molecule breaks into the radical products $H + HCO$. The PO identified with this event is associated with the centrifugal barrier (and is referred to as a “relative equilibrium” or “relative periodic orbit” in the mathematics literature) and has been labeled PO_{OTS} in Figure 2. This PO is at a large value of R , with R essentially constant and with θ making a full cycle from 0 to 2π . In other words, the roaming hydrogen atom rotates around the HCO fragment at a large value of R . A second reactive event occurs when the system escapes from the formaldehyde well and reaches the flat region of the PES. In our model, this occurs for R at around 6–8 au and θ in the region of 0–2 rad.

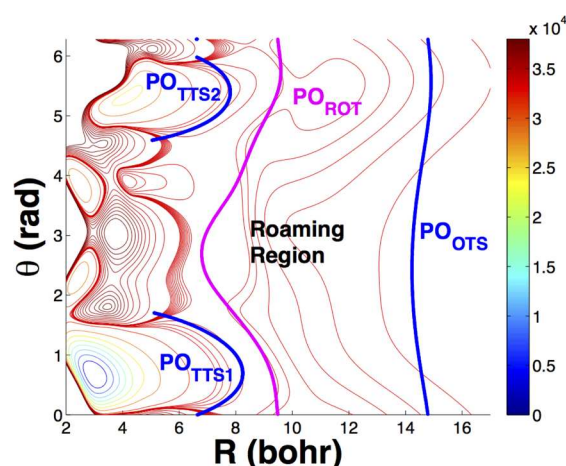


Figure 2. POs from which DSs that describe different reactive events in formaldehyde decomposition are constructed as well as resonant (also orbiting) PO in the roaming region. The energy units are cm^{-1} .

We have located an unstable PO that defines the DS for passage from formaldehyde to the complex $\text{HCO}\cdots\text{H}$. This PO has been labeled PO_{TTS1} in Figure 2. The final reactive event that we consider consists of the binding of the two hydrogen atoms just before the molecule breaks into the molecular products, $\text{H}_2 + \text{CO}$. The PO defining the DS for this event is similar to the

one just described and is located in approximately the same range of the R coordinate with θ varying from 4.5 to 6 rad and has been labeled PO_{TTS2} in Figure 2. Figure 2 shows the projections of these 3 POs into configuration space along with the contours of the PES and a PO labeled PO_{ROT} (magenta curve) that will be discussed below.

Each of the POs is 1D and defines a 2D DS. Ignoring overall rotation in the plane, the molecular phase space is four-dimensional, so that the DS serves to partition the 3D constant energy surface. Each of the three POs that we have identified belongs to a family of POs that exists for a range of energies. For our study, we have located the POs at an energy just above the threshold for the radical products $\text{H} + \text{HCO}$. For our model, this threshold is at 33558 cm^{-1} , and the energies of the POs have been taken to be 200 cm^{-1} above this threshold. The DSs constructed from the POs are surfaces in phase space at the same total energy of the POs. The DSs consist of two parts, one which intersects trajectories that evolve from reactants to products (forward) and the other which intersects trajectories that evolve from products to reactants (backward).

We have constructed the DS attached to PO_{TTS1} associated with the reactive event $\text{H}_2\text{CO} \rightarrow \text{HCO}\cdots\text{H}$. Our algorithm to sample points of the DS is explained in the SI. Figure 3a shows the projection of the reactant-to-product half (i.e., hemisphere) of this DS on the space (θ, p_θ, p_R) with PO_{TTS1} depicted as a magenta line. This DS hemisphere intersects *all* trajectories

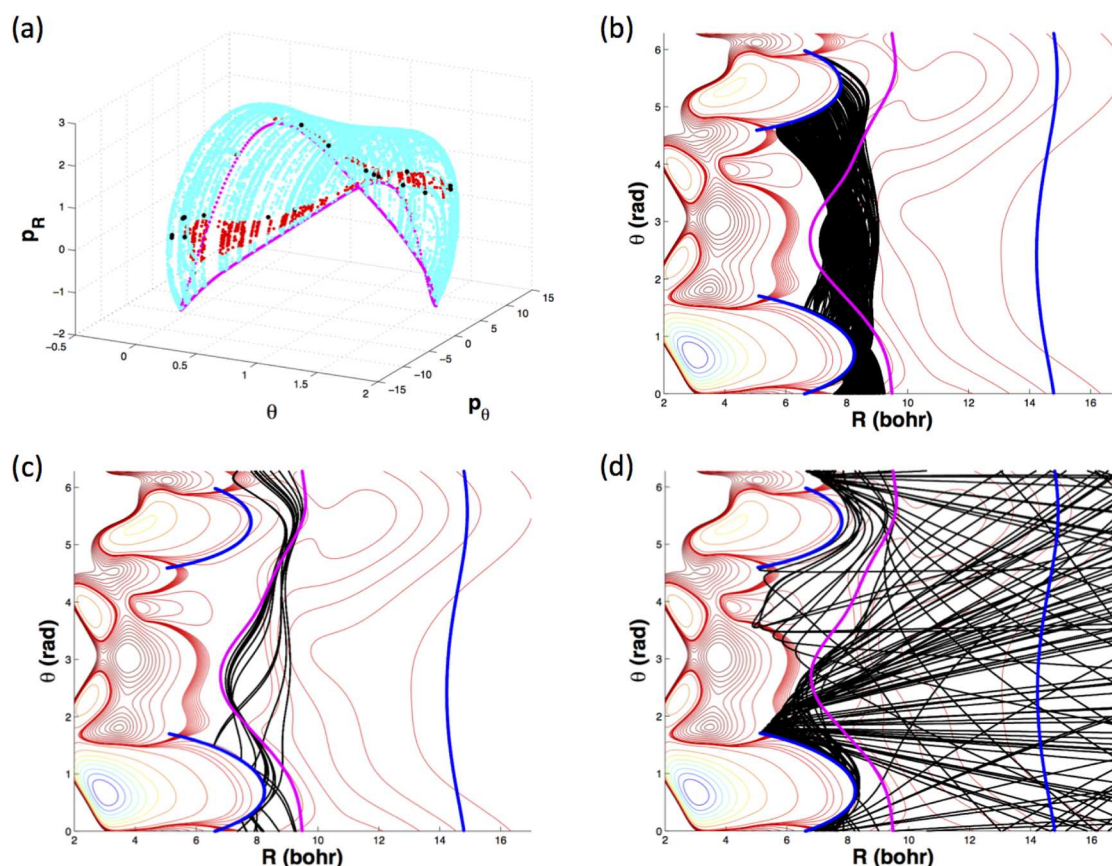


Figure 3. Trajectory propagation from the DS. (a) We show 9846 initial conditions on the DS. Initial conditions corresponding to the three types of trajectories (see text) have been assigned different colors. Red denotes initial conditions for roaming trajectories (669 initial conditions), black denotes initial conditions corresponding to trajectories that return to the formaldehyde well (22 initial conditions), and cyan denotes initial conditions corresponding to $\text{H} + \text{HCO}$ trajectories, that is, dissociating trajectories (9155 initial conditions). The next three panels illustrate some trajectories of each type. (b) Roaming trajectories. (c) Trajectories returning to the formaldehyde well. (d) $\text{H} + \text{HCO}$ trajectories.

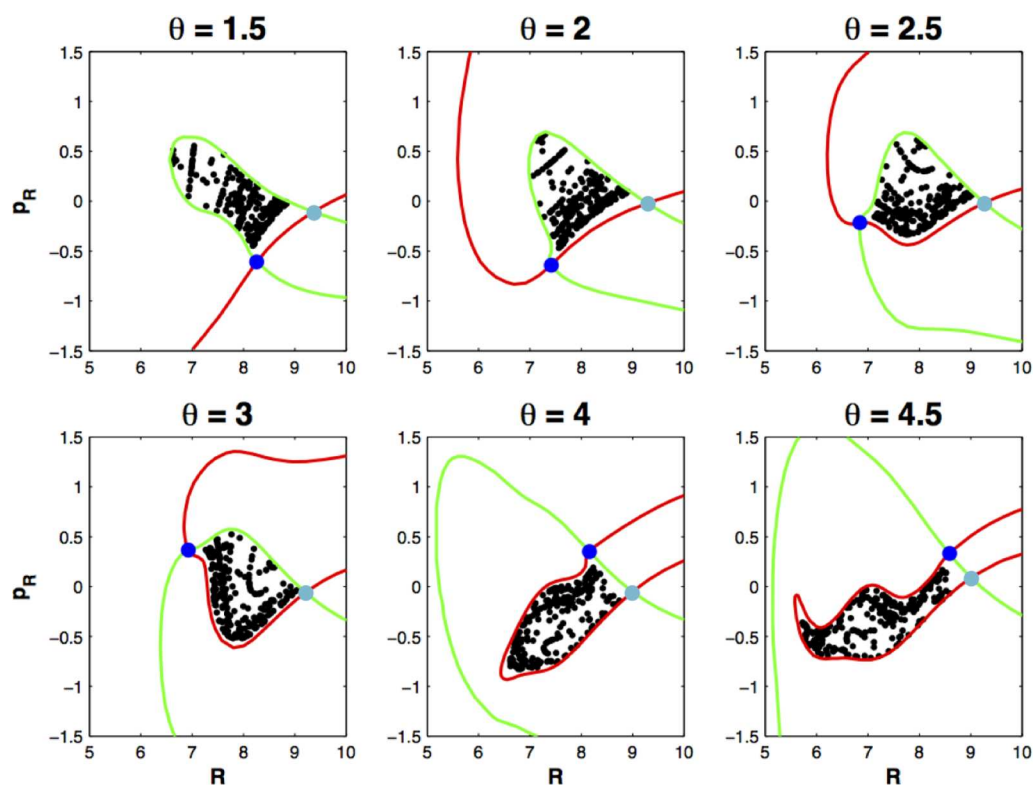


Figure 4. Stable and unstable invariant manifolds of the PO in the roaming region on different PSS located at various values of θ (the value of θ is shown above each panel). The stable manifold is shown in green and the unstable manifold in red. The blue (cyan) bullet is the intersection of the orbiting periodic orbit (homoclinic orbit) with the plane of section (see text). Black dots represent crossings of the different PSS by the roaming trajectories.

undergoing the reaction $\text{H}_2\text{CO} \rightarrow \text{HCO}\cdots\text{H}$. To investigate the dynamics of formaldehyde dissociation, we sampled this DS hemisphere (see the SI) and initiated trajectories at the sampled points. We then propagated the trajectories until they crossed the DSs associated with the other POs (or the same PO). We focus on roaming trajectories initiated on the DS controlling the escape from the formaldehyde well and ending up in the $\text{H}_2\cdots\text{CO}$ well by crossing the DS associated with $\text{PO}_{\text{TTS}2}$ (Figure 3b). Similarly, the system has completed the reaction $\text{HCO}\cdots\text{H} \rightarrow \text{H}_2\text{CO}$, when the trajectories cross the backward DS associated with $\text{PO}_{\text{TTS}1}$ (Figure 3c). Finally, the reaction $\text{HCO}\cdots\text{H} \rightarrow \text{H} + \text{HCO}$ occurs when the system crosses the DS associated with PO_{OTS} at a large value of R (Figure 3d).

Therefore, for trajectories initiated on the DS controlling the escape from the formaldehyde well, there are three possible outcomes: the roaming behavior just described, a return to the formaldehyde well by recrossing the other hemisphere of the DS from which they were initiated, and dissociation to the radical product by crossing the DS at a large value of R . The phase space DS associated with $\text{PO}_{\text{TTS}1}$ intersects *all* trajectories that escape the formaldehyde well, and all three possibilities occur. It should be noted that those trajectories that end up dissociating to $\text{H} + \text{HCO}$ can exhibit several turning points in R with an extended range in angle θ before crossing the DS at large R ; such trajectories orbit around HCO before producing the radical products.

We now consider the dynamical “mechanism” that causes roaming trajectories to turn in the θ direction instead of evolving directly to the radical products. To identify the mechanism, we must consider the dynamics in the region

where a trajectory has the three possible fates. This is the region bounded by the three DSs associated with the three POs $\text{PO}_{\text{TTS}1}$, $\text{PO}_{\text{TTS}2}$, and PO_{OTS} discussed above. These DSs bound a region in phase space that is the roaming region, associated with the flat region of the PES, and this is the location where the dynamical complex $\text{HCO}\cdots\text{H}$ is defined.^{30,31} In this region, the molecule is not yet dissociated, and couplings between the two degrees of freedom are still present, which enable the system to transfer energy between these DoF. Note that there is no arbitrariness in our definition of the roaming region once we have identified the relevant DSs.

Figure 3b shows a relatively small spread of roaming trajectories in configuration space, in the R range of [6.5, 9.5] au. The roaming trajectories appear to approximately follow the nearby orbiting periodic orbit PO_{ROT} , also shown as a magenta curve (as in Figure 2). We show, in Figure 1 of the SI, a few trajectories from the ensemble of trajectories in Figure 3b. From PO_{ROT} , which passes directly through the roaming region, emerge the phase space structures that cause the H atom to roam.

We analyze the behavior of trajectories in the vicinity of PO_{ROT} by computing 2D surfaces in phase space (the stable and unstable invariant manifolds) associated with PO_{ROT} . These surfaces can intersect to form a phase space conduit that envelopes the roaming trajectories and leads them to particular regions of phase space.³⁸ In the case of formaldehyde, we will see that this phase space shepherding is the mechanism for transferring energy from the radial to the angular mode.

To visualize the shape of the phase space conduit composed of segments of the stable and unstable manifolds of PO_{ROT} , we construct Poincaré surfaces of section (PSS) by fixing one of

the two coordinates and recording every time a trajectory crosses the plane. These plots provide a well-known method to explore the phase space structures in 2 DoF dynamical systems.

To show the role of the invariant stable and unstable manifolds of PO_{ROT} , we plot in Figure 4 pieces of these manifolds (green for the stable and red for the unstable) on several PSS constructed by fixing θ at different values and taking $p_\theta > 0$. Along with these manifolds on the different PSS, we also plot the traces that the roaming trajectories leave on the plane (black dots). The blue bullet marks the intersection of PO_{ROT} with the PSS. This figure strikingly reveals the influence of these manifolds on the roaming trajectories; they are trapped in a region bounded by the stable and unstable manifolds of the PO and extending to the intersection point of the stable and unstable manifolds of PO_{ROT} (depicted by the cyan bullet), which is referred to as a homoclinic point. The area confined by the stable and unstable manifolds of PO_{ROT} is conserved, but it does change shape as θ varies. In fact, Figure 4 shows that as θ increases, this region deforms and moves toward the DS controlling the access to the $H_2\cdots CO$ well. This is the phase space mechanism for energy to be transferred between the two DoFs and for trajectories to be shepherd from the formaldehyde well, through the roaming region, and into the $H_2\cdots CO$ well.

We have considered the prototypical roaming reaction—hydrogen atom roaming in formaldehyde decomposition—from a phase space perspective. We have constructed DSs in phase space that are bottlenecks associated with the relevant reactive events and that enable us to define the roaming region dynamically. These DSs have the “no-recrossing” and minimal flux properties. We are thereby able to sample the DS associated with escape from the formaldehyde well and determine how these particular trajectories evolve throughout the roaming region and undergo the different reactive events. The phase space perspective allows us to determine why trajectories roam rather than dissociate through the radical channel. It turns out that in the roaming region, there is an unstable PO, PO_{ROT} , whose stable and unstable manifolds trap all roaming trajectories that exit the formaldehyde well and shepherd them toward the $H_2\cdots CO$ well. This finding provides a very compelling dynamical explanation for roaming in formaldehyde.

Roaming in formaldehyde has been treated by statistical theories.^{39,40} Our analysis indicates that the dynamics in the roaming region is nonstatistical, as is evidenced by the distributions of the different types of trajectories in Figure 3a. As the basic assumptions of TST are not fulfilled in the roaming region, resorting to a dynamical approach to predict rates for this system may be required. Nonstatisticality in roaming dynamics in formaldehyde will be explored further in a future paper.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.5b01930.

Hamiltonian and PES for the model and DS associated with a PO (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Townsend, D.; Lahankar, S. A.; Lee, S. K.; Chambreau, S. D.; Suits, A. G.; Zhang, X.; Rheinecker, J.; Harding, L. B.; Bowman, J. M. The Roaming Atom: Straying from the Reaction Path in Formaldehyde decomposition. *Science* **2004**, *306*, 1158–1161.
- (2) van Zee, R. D.; Foltz, M. F.; Moore, C. B. Evidence for a Second Molecular Channel in the Fragmentation of Formaldehyde. *J. Chem. Phys.* **1993**, *99*, 1664–1673.
- (3) Hause, M. L.; Herath, N.; Zhu, R.; Lin, M. C.; Suits, A. G. Roaming-Mediated Isomerization in the Photodissociation of Nitrobenzene. *Nat. Chem.* **2011**, *3*, 932–937.
- (4) Lee, K. L. K.; Quinn, M. S.; Maccarone, A. T.; Nauta, K.; Houston, P. L.; Reid, S. A.; Jordan, M. J. T.; Kable, S. H. Two Roaming Pathways in the Photolysis of CH_3CHO between 328 and 308 nm. *Chem. Sci.* **2014**, *5*, 4633–4638.
- (5) Sivaramakrishnan, R.; Michael, J. V.; Wagner, A. F.; Dawes, R.; Jasper, A. W.; Harding, L. B.; Georgievskii, Y.; Klippenstein, S. J. Roaming Radicals in the Thermal Decomposition of Dimethyl Ether: Experiment and Theory. *Combust. Flame* **2011**, *158*, 618–632.
- (6) Bowman, J. M.; Shepler, B. C. Roaming Radicals. *Annu. Rev. Phys. Chem.* **2011**, *62*, 531–553.
- (7) Grubb, M. P.; Warter, M. L.; Xiao, H.; Maeda, S.; Morokuma, K.; North, S. W. No Straight Path: Roaming in Both Ground- and Excited-State Photolytic Channels of $NO_3 \rightarrow NO + O_2$. *Science* **2012**, *335*, 1075–1077.
- (8) Ulusoy, I. G.; Stanton, J. F.; Hernandez, R. Effects of Roaming Trajectories on the Transition State Theory Rates of a Reduced-Dimensional Model of Ketene Isomerization. *J. Phys. Chem. A* **2013**, *117*, 7553–7560.
- (9) Ulusoy, I. G.; Stanton, J. F.; Hernandez, R. Correction to ‘Effects of Roaming Trajectories on the Transition State Theory Rates of a Reduced-Dimensional Model of Ketene Isomerization’. *J. Phys. Chem. A* **2013**, *117*, 10567–10568.
- (10) Heidrich, D. Ed. *The Reaction Path in Chemistry: Current Approaches and Perspectives*; Springer: New York, 1995.
- (11) Sun, L. P.; Song, K. Y.; Hase, W. L. A SN_2 Reaction that Avoids Its Deep Potential Energy Minimum. *Science* **2002**, *296*, 875–878.
- (12) Lopez, J. G.; Vayner, G.; Lourderaj, U.; Addepalli, S. V.; Kato, S.; Dejong, W. A.; Windus, T. L.; Hase, W. L. A Direct Dynamics Trajectory Study of $F^- + CH_3OOH$ Reactive Collisions Reveals a Major Non-IRC Reaction Path. *J. Am. Chem. Soc.* **2007**, *129*, 9976–9985.
- (13) Mikosch, J.; Trippel, S.; Eichhorn, C.; Otto, R.; Lourderaj, U.; Zhang, J. X.; Hase, W. L.; Weidemüller, M.; Wester, R. Imaging Nucleophilic Substitution Dynamics. *Science* **2008**, *319*, 183–186.
- (14) Zhang, J.; Mikosch, J.; Trippel, S.; Otto, R.; Weidemüller, M.; Wester, R.; Hase, W. L. $F^- + CH_3I \rightarrow FCH_3 + I^-$ Reaction Dynamics. Nontraditional Atomistic Mechanisms and Formation of a Hydrogen-Bonded Complex. *J. Phys. Chem. Lett.* **2010**, *1*, 2747–2752.
- (15) Mohammad, F.; Morris, V. R.; Fink, W. H.; Jackson, W. M. On the Mechanism and Branching Ratio of the $CN + O_2 \rightarrow CO + NO$ Reaction Channel Using Transient IR Emission Spectroscopy. *J. Phys. Chem.* **1993**, *97*, 11590–11598.
- (16) Polanyi, J. C.; Schreiber, J. L.; Skrlac, W. J. Distribution of Reaction Products (Theory). Part 12. ‘Microscopic Branching in $H + XY \rightarrow HX + Y$, $HY + X$ ($X, Y = \text{Halogens}$). *Faraday Discuss. Chem. Soc.* **1979**, *67*, 66–89.

- (17) Wigner, E. P. The Transition State Method. *Trans. Faraday Soc.* **1938**, *34*, 29–40.
- (18) Wigner, E. P. Some Remarks on the Theory of Reaction Rates. *J. Chem. Phys.* **1939**, *7*, 646–650.
- (19) Pechukas, P. Transition State Theory. *Annu. Rev. Phys. Chem.* **1981**, *32*, 159–177.
- (20) Levine, R. D. *Molecular Reaction Dynamics*; Cambridge University Press: Cambridge, U.K., 2009.
- (21) Carpenter, B. K. *Determination of Organic Reaction Mechanisms*; Wiley: New York, 1984.
- (22) Wales, D. J. *Energy Landscapes*; Cambridge University Press: Cambridge, U.K., 2003.
- (23) Shepler, B. C.; Han, Y.; Bowman, J. M. Are Roaming and Conventional Saddle Points for H_2CO and CH_3CHO Dissociation to Molecular Products Isolated from Each Other? *J. Phys. Chem. Lett.* **2011**, *2*, 834–838.
- (24) Harding, L. B.; Klippenstein, S. J.; Jasper, A. W. Separability of Tight and Roaming Pathways to Molecular Decomposition. *J. Phys. Chem. A* **2012**, *116*, 6967–6982.
- (25) Waalkens, H.; Schubert, R.; Wiggins, S. Wigner's Dynamical Transition State Theory in Phase Space: Classical and Quantum. *Nonlinearity* **2007**, *21*, R1–R118.
- (26) Wiggins, S. *Normally Hyperbolic Invariant Manifolds in Dynamical Systems*; Springer-Verlag: New York, 1994.
- (27) Ezra, G. S.; Waalkens, H.; Wiggins, S. Microcanonical Rates, Gap Times, and Phase Space Dividing Surfaces. *J. Chem. Phys.* **2009**, *130*, 164118.
- (28) Wiggins, S. *Introduction to Applied Nonlinear Dynamical Systems and Chaos* 2nd ed.; Springer-Verlag: New York, 2003.
- (29) Chesnavich, W. J. Multiple Transition States in Unimolecular Reactions. *J. Chem. Phys.* **1986**, *84*, 2615.
- (30) Mauguire, F. A. L.; Collins, P.; Ezra, G. S.; Farantos, S. C.; Wiggins, S. Multiple Transition States and Roaming in Ion–Molecule Reactions: a Phase Space Perspective. *Chem. Phys. Lett.* **2014**, *592*, 282–287.
- (31) Mauguire, F. A. L.; Collins, P.; Ezra, G. S.; Farantos, S. C.; Wiggins, S. Roaming Dynamics in Ion–Molecule Reactions: Phase Space Reaction Pathways and Geometrical Interpretation. *J. Chem. Phys.* **2014**, *140*, 134112.
- (32) Mauguire, F. A. L.; Collins, P.; Ezra, G. S.; Farantos, S. C.; Wiggins, S. Roaming Dynamics in Ketene Isomerization. *Theor. Chem. Acc.* **2014**, *133*, 1–13.
- (33) Chesnavich, W. J.; Bowers, M. T. *Theory of Ion-Neutral Interactions: Application of Transition State Theory Concepts to Both Collisional and Reactive Properties of Simple Systems*; Pergamon Press: Oxford, U.K., 1982.
- (34) Miller, W. H. Unified Statistical Model for Complex and Direct Reaction Mechanisms. *J. Chem. Phys.* **1976**, *65*, 2216–2223.
- (35) Wiesenfeld, L. Geometry of Phase Space Transition States: Many Dimensions, Angular Momentum. *Advances in Chemical Physics*; John Wiley & Sons: Hoboken, NJ, 2005; Vol. 130, pp 217–265.10.1002/0471712531.ch4
- (36) Suits, A. G. Roaming Atoms and Radicals: A New Mechanism in Molecular Dissociation. *Acc. Chem. Res.* **2008**, *41*, 873–881.
- (37) Zhang, X.; Zou, S.; Harding, L. B.; Bowman, J. M. A Global Ab Initio Potential Energy Surface for Formaldehyde. *J. Phys. Chem. A* **2004**, *108*, 8980–8986.
- (38) MacKay, R. S.; Meiss, J. D.; Percival, I. C. Transport in Hamiltonian Systems. *Phys. D* **1984**, *13*, 55–81.
- (39) Klippenstein, S. J.; Georgievskii, Y.; Harding, L. B. Statistical Theory for the Kinetics and Dynamics of Roaming Reactions. *J. Phys. Chem. A* **2011**, *115*, 14370–14381.
- (40) Andrews, D. U.; Kable, S. H.; Jordan, M. J. T. A Phase Space Theory for Roaming Reactions. *J. Phys. Chem. A* **2013**, *117*, 7631–7642.